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The Crystal Structure of a Monoclinic Form of Aluminium Metaphosphate, $Al(PO_3)_3$

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$Al(PO_3)_3$ crystallizes in the monoclinic space group Ic with $a=10{\cdot}423$, $b=18{\cdot}687$, $c=9{\cdot}222$ Å, $\beta=81{\cdot}63°$; $Z=12$. In the [010] direction a subcell structure is present with a period of $b/3$. The structure was solved from the Patterson function. It can be described as a network of Al octahedra and P tetrahedra. Infinite chains of tetrahedra run along [001] interconnected by octahedra, the repeat distance in the chain being six tetrahedra. The mean Al–O distance in the octahedra is 1·884 Å; the P–O bonds which are linked to octahedra have a mean value of 1·483 Å; those connected to other tetrahedra are 1·577 Å.

Introduction

Cubic $Al(PO_3)_3$ was first described by Hautefeuille & Margottet (1883). This form has been investigated by Hendricks & Wyckoff (1927) (space group), Pauling & Sherman (1937) (structure determination), Wappler (1958) (refinement) and Kleber (1960) (growth forms). Other crystalline metaphosphates are reported by d'Yvoire (1960).

The observation of Hautefeuille & Margottet that mixed crystals could be prepared with various quantities of Cr, Fe and U, whose metaphosphates are reported as orthorhombic, was the motive for investigating the existence of forms other than cubic. Visser (1962) pointed out the resemblance of the powder diagram of the monoclinic form to that of monoclinic $Fe(PO_3)_3$. The cell constants of the Fe compound are $a=13{\cdot}137$, $b=19{\cdot}083$, $c=9{\cdot}395$ Å, $\beta=126{\cdot}95°$, which suggest isomorphism. Here the crystal structure of monoclinic $Al(PO_3)_3$ is presented.

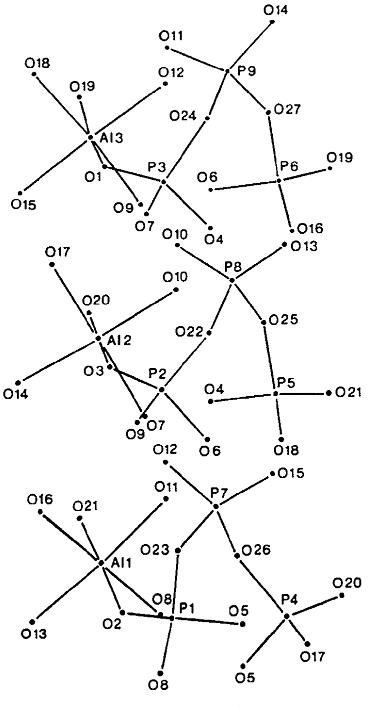

Fig. 1. Numbering of the atoms.

Experimental

Crystals suitable for X-ray investigation were prepared by melting Al_2O_3 and HPO_3 in a Pt crucible. Cell constants were obtained from zero-level Weissenberg photographs calibrated with Al powder lines: $a=10{\cdot}423$ (3), $b=18{\cdot}687$ (2), $c=9{\cdot}222$ (1) Å, $\beta=81{\cdot}63$ (1)°.

The space group is Ic or $I2/c$; the structure determination has shown the first to be correct. The crystals just sank in bromoform; the density therefore is about 2·90, whereas with $Z=12$, 2·96 g cm^{-3} is calculated.

Intensities were measured with a Nonius automatic single-crystal diffractometer AD3, operating in the ω-scan mode. Two sets of intensities were collected, one with Cu $K\alpha$ giving 967, the other with Mo $K\alpha$ radiation yielding 3752 observed non-zero intensities. In the data obtained with Cu radiation an intensity difference attributable to absorption could be observed between symmetry-equivalent reflexions; the other set did not show this. Therefore, the refinement has been carried out with the Mo measurements without absorption correction.

Structure determination

From an inspection of the intensities it was apparent that a subcell structure was present. The reflexions with $k=3n\pm1$ were weak, suggesting a tripartitioning of b. Thus the structure determination was divided into two stages. First the average subcell structure was determined and after this the full crystal structure by deriving the deviations of the atoms from the average positions. The most probable space group is Ic since in this case the atoms of the 12 formula units in the cell can be placed at three sets of general positions.

A Patterson function was calculated from the 368 reflexions with $k=3n$ from the set of Cu $K\alpha$ data, transformed to a reduced cell. The orientation of the

Al octahedron was found from the Al–O vectors on the sphere with radius 1·8 Å around the origin. It can be expected that Al octahedra and P tetrahedra are connected in such a way that the angle Al–O–P is near 180°. As the Al–O and P–O lengths are 1·8 and 1·5 Å, it is assumed that the Al–P vectors will be found in the Patterson function on a sphere around the origin with a radius of about 3 Å.

When these vectors had been found, the Al–O–P triangle could be completed and the position of the O–P vectors located on the sphere with radius 1·4 Å. From the knowledge of the orientation and connexion of octahedra and tetrahedra thus found, a model of the average structure was constructed.

The subcell structure, an average of three sets of positions, was refined by least squares with the $k=3n$ subset of reflexions. Since the intensities with $k=3n$ must also contain information about the deviations from the average positions, a difference synthesis was calculated with these reflexions. This difference map gave indications for offsetting six of the nine P atoms from their average positions. This proved to be sufficient for starting the refinement of the full structure. It was not possible to refine all atoms with individual anisotropic temperature factors in an unrestricted full-matrix refinement due to limitations in the program. Therefore in the final refinement the Al plus the P atoms and the O atoms were refined alternately, the thermal parameters of corresponding atoms in the three subcells

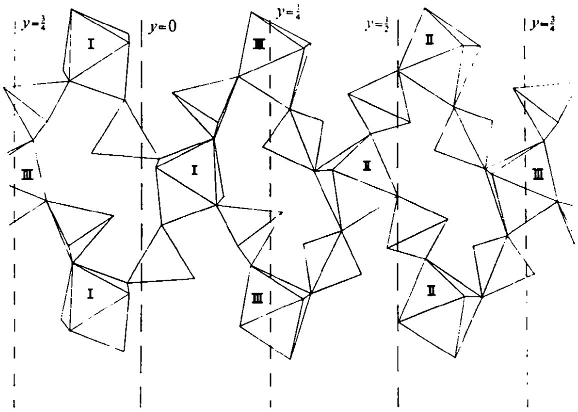

Fig. 2. yz plane at $x=\frac{1}{2}$.

Table 1. *Fractional coordinates* ($\times 10^4$) *and thermal parameters* ($\times 10^5$)

The standard deviation of each coordinate from refinement is 0·004, 0·003 and 0·007 Å for Al, P and O respectively.

	x	y	z	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{31}$
Al(1)	5073	878	67	602	561	346	−45	19	−43
Al(2)	5053	4202	57						
Al(3)	4867	7452	−72						
P(1)	6473	276	7010	506	337	241	−42	49	53
P(2)	6310	3646	6889						
P(3)	6289	6969	6840						
P(4)	8756	310	3182	535	601	463	88	−14	−111
P(5)	8573	3635	3107						
P(6)	8617	6986	3065						
P(7)	7317	1486	4930	526	329	439	−51	−160	30
P(8)	7688	4848	5121						
P(9)	7560	8183	5081						
O(1)	179	2130	2994	777	808	489	310	−401	534
O(2)	501	5353	3342						
O(3)	295	8908	3071						
O(4)	2244	1460	2522	859	1124	1194	571	184	−720
O(5)	2884	5224	2449						
O(6)	2246	8110	2562						
O(7)	964	1632	484	1143	837	552	−247	−252	−243
O(8)	1262	4695	1000						
O(9)	885	8295	597						
O(10)	1580	245	9706	946	1802	897	532	81	−160
O(11)	1365	3430	9521						
O(12)	1334	6959	9418						
O(13)	3729	255	674	1234	157	839	−759	−241	−143
O(14)	3475	3714	537						
O(15)	3467	6824	431						
O(16)	3888	1438	9139	1146	956	610	758	745	−9
O(17)	4131	5003	9546						
O(18)	3714	8126	9321						
O(19)	4625	2123	6777	1316	650	464	580	−99	336
O(20)	4857	5524	7034						
O(21)	4637	8637	6857						
O(22)	2250	715	6379	1286	1022	1008	1217	−436	−168
O(23)	1584	3985	6194						
O(24)	2157	7340	6434						
O(25)	3340	589	3747	1474	649	747	−178	755	398
O(26)	2756	4055	3627						
O(27)	3376	7270	3857						

being constrained to the same value. The refinement, in which a Cruickshank (1961) weighting scheme was used, was terminated at $R=0{\cdot}057$ for 3752 observed reflexions. The final coordinates and thermal parameters are presented in Table 1.*

From the error estimates in the refinement, the errors in the coordinates can be set at about 0·004, 0·003 and 0·007 Å for Al, P and O respectively. The numbering of the atoms is given in Fig. 1.

Description of the structure

In Table 2 the bond distances and angles are presented. The estimated standard deviations from the least-squares refinement are about 0·008 Å for the Al–O and P–O distances and 0·4° for the O–Al–O and O–P–O angles. Since these figures are underestimates and should be multiplied by at least a factor of two, it may be concluded that Al octahedra probably do not deviate from regularity. The mean of the Al–O distances is 1·884 (5) Å. The Al–O distances may be compared with those reported in other structures, *e.g.* wavellite, $Al(PO_4)_2(OH)_3.4\frac{1}{2}–5H_2O$ (Araki & Zoltai, 1968); eosphorite, $AlPO_4(Mn,Fe)(OH)_2.H_2O$ (Hanson, 1960); and turquois, $CuAl_6(PO_4)_4(OH)_8.4H_2O$ (Cid-

Table 2. *Bond distances and angles*

A(1)-O(2)	1·87	Al(2)-O(3)	1·89	Al(3)-O(1)	1·86
-O(8)	1·93	-O(7)	1·90	-O(9)	1·91
-O(11)	1·88	-O(10)	1·89	-O(12)	1·89
-O(13)	1·85	-O(14)	1·88	-O(15)	1·88
-O(16)	1·91	-O(17)	1·88	-O(18)	1·88
-O(21)	1·88	-O(20)	1·88	-O(19)	1·87
P(1)-O(2)	1·48	P(2)—O(3)	1·49	P(3)—O(1)	1·48
-O(5)	1·58	-O(6)	1·59	-O(4)	1·57
-O(8)	1·47	-O(9)	1·48	-O(7)	1·48
-O(23)	1·57	-O(22)	1·57	-O(24)	1·59
P(4)-O(5)	1·57	P(5)—O(4)	1·57	P(6)—O(6)	1·58
-O(17)	1·48	-O(18)	1·49	-O(16)	1·48
-O(20)	1·50	-O(21)	1·48	-O(19)	1·49
-O(26)	1·59	-O(25)	1·57	-O(27)	1·57
P(7)-O(12)	1·48	P(8)—O(10)	1·47	P(9)—O(11)	1·49
-O(15)	1·49	-O(13)	1·48	-O(14)	1·48
-O(23)	1·57	-O(22)	1·58	-O(24)	1·59
-O(26)	1·59	-O(25)	1·58	-O(27)	1·56
O(2)—Al(1)-O(8)	90	O(3)—Al(2)-O(7)	88	O(1)—Al(3)-O(9)	93
-O(11)	94	-O(10)	90	-O(12)	86
-O(13)	90	-O(14)	94	-O(15)	93
-O(16)	90	-O(17)	89	-O(18)	88
-O(21)	177	-O(20)	178	-O(19)	173
O(8)- -O(11)	91	O(7)- -O(10)	93	O(9)- -O(12)	92
-O(13)	91	-O(14)	90	-O(15)	85
-O(16)	180	-O(17)	177	-O(18)	174
-O(21)	88	-O(20)	90	-O(19)	91
O(11)- -O(13)	176	O(10)- -O(14)	175	O(12)- -O(15)	177
-O(16)	89	-O(17)	88	-O(18)	94
-O(21)	89	-O(20)	89	-O(19)	89
O(13)- -O(16)	88	O(14)- -O(17)	89	O(15)- -O(18)	89
-O(21)	88	-O(20)	86	-O(19)	92
O(16)- -O(21)	92	O(17)- -O(20)	92	O(18)- -O(19)	89
O(2)—P(1)—O(5)	110	O(3)—P(2)—O(6)	109	O(1)—P(3)—O(4)	108
-O(8)	117	-O(9)	118	-O(7)	116
-O(23)	108	-O(22)	108	-O(24)	111
O(5)- -O(8)	110	O(6)- -O(9)	108	O(4)- -O(7)	108
-O(23)	100	-O(22)	102	-O(24)	102
O(8)- -O(23)	111	O(9)- -O(22)	110	O(7)- -O(24)	110
O(5)—P(4)—O(17)	111	O(4)—P(5)—O(18)	112	O(6)—P(6)—O(16)	113
-O(20)	107	-O(21)	109	-O(19)	110
-O(26)	101	-O(25)	98	-O(27)	98
O(17)- -O(20)	116	O(18)- -O(21)	116	O(16)- -O(19)	118
-O(26)	108	-O(25)	109	-O(27)	110
O(20)- -O(26)	113	O(21)- -O(25)	110	O(19)- -O(27)	105
O(12)-P(7)—O(15)	118	O(10)-P(8)—O(13)	118	O(11)-P(9)—O(14)	120
-O(23)	107	-O(22)	112	-O(24)	109
-O(26)	106	-O(25)	108	-O(27)	108
O(15)- -O(23)	110	O(13)- -O(22)	104	O(14)- -O(24)	107
-O(26)	110	-O(25)	107	-O(27)	105
O(23)- -O(26)	105	O(22)- -O(25)	107	O(24)- -O(27)	107

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31762 (17 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Dresdner, 1965); in these structures the comparable Al–O distances range from 1·834 to 1·927 Å.

The P–O bonds connected to octahedra are about 0·1 Å shorter than the bonds to other tetrahedra. The mean of the short bonds is 1·483 (2) Å, that of the longer ones 1·577 (2) Å. The same is found in other metaphosphates, *e.g.* $(RbPO_3)_\infty$ (Cruickshank, 1964); $CuLi(PO_3)_3$ (Laügt, Tordjman, Guitel & Roudaut, 1972); $CuNa_2(PO_3)_4$ (Läugt, Tordjman, Guitel & Bassi, 1972); $[Na_3H(PO_3)_4]_x$ (Jost, 1968); $(NaPO_3)_x$ (McAdam, Jost & Beagley, 1968); and $Ba_2K(PO_3)_5$ (Martin, Tordjman & Mitschler, 1972), where these distances fall in the ranges of 1·45–1·51 and 1·58–1·62 Å. The mean bond angle between the shorter bonds in the tetrahedra is 117·5 (5)°. The angle between the longer bonds in the tetrahedra around P(7), P(8) and P(9) is different from those in the other tetrahedra; the respective means are 106·2 (5) and 100·2 (7)°. In the literature cited, values between 99 and 102° are found. The structure consists of infinite chains of tetrahedra interconnected by Al octahedra. Each octahedron shares corners with six tetrahedra and two octahedra.

The manner in which the Al octahedra and P tetrahedra link together is made clear in Figs. 2, 3 and 4; the octahedra are marked I, II and III in order to discriminate between the three different octahedra stemming from the three subcell parts.

In Fig. 2 a view of the *yz* plane around $x=\frac{1}{2}$ is given in which a network of alternating octahedra and tetrahedra exists. The connexion in the direction of *x* is illustrated in Fig. 3, showing a picture of the *xy* plane around $z=0$. Chains of alternating octahedra and tetrahedra run in the *x* direction only. Along the *a* glide plane at $y=\frac{3}{4}$ the chain is formed solely from type III octahedra. In the other two chains octahedra I and II alternate; the *a* glide plane at $y=\frac{1}{4}$ interrelates these two. In a partial projection on the *yz* plane in Fig. 4 the infinite chains of P tetrahedra running along [001] are indicated.

The repeat unit consists of six tetrahedra. Infinite chains of tetrahedra with a period of six tetrahedra are also found in $CuLi(PO_3)_3$ where they form a helix around a twofold screw axis. In contrast to this the chain in $Al(PO_3)_3$ describes a 'figure 8' when seen in projection along *z*. Al octahedra are linked to the chain, four tetrahedra forming a loop across an octahedron edge.

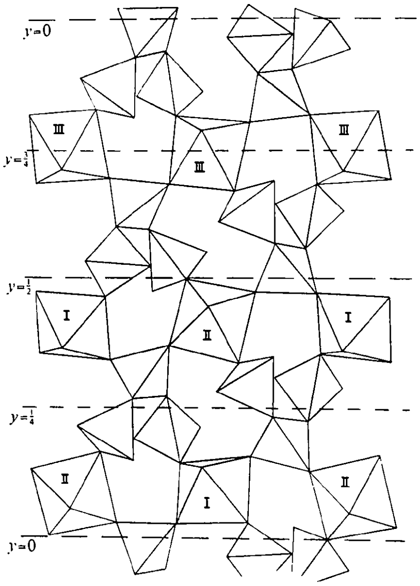

Fig. 3. *xy* plane at $z=0$.

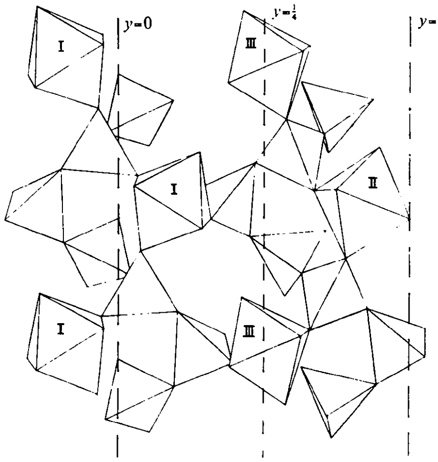

Fig. 4. Chains of tetrahedra in the *z* direction.

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